



Atmospheric Environment 38 (2004) 6867–6874

**ATMOSPHERIC  
ENVIRONMENT**[www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)

# Phosphine and methylphosphine production by simulated lightning—a study for the volatile phosphorus cycle and cloud formation in the earth atmosphere

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Received 3 March 2004; accepted 23 August 2004

## Abstract

Phosphine (PH<sub>3</sub>), was recently found worldwide even in the remote atmosphere (Naturwissenschaften 83(1996a)131; Atmos. Environ. 37(2003)2429). It is of interest to find natural mechanisms which could produce phosphine gas and drive a volatile link of the atmospheric phosphorus cycle and the formation of phosphoric acid as possible condensation nuclei for clouds.

Here, we report on simulated lightning exposing sodium phosphate in a reducing medium (methane model atmosphere or organic matter) for 5 s to a spark induced by microwave. The gas product analyzed by gas chromatography contained phosphine (yield up to 0.6 g kg<sup>-1</sup> phosphate P) and methylphosphine (CH<sub>3</sub>)PH<sub>2</sub> (yield up to 0.02 g kg<sup>-1</sup> phosphate P).

We suggest a plasma-chemical formation mechanism where organic compounds or methane or secondary hydrogen thereof reduce phosphate to phosphine of which a small fraction can subsequently react with methyl radicals to form methylphosphine. A small yield of 6 mg phosphine per kg phosphate P was even obtained in methane free medium, by simple plasmatic recombination of inorganic phosphorus. We believe that methane and hydrogen are useful model substances of pyrolytic gases with high reducing power which may form if lightning strikes biomass, soil and aerosol.

These results suggest evidence that phosphine and methylphosphine (detectable in the field by intense garlic odor) are produced when atmospheric lightning strikes the ground or aerosol which is containing oxidized forms of phosphorus and chemical reductants.

Additional reviewed data show that laboratory lightning was able to reduce a much more significant portion of phosphate to phosphite (up to 25% yield), methylphosphonic acid (up to 8.5% yield) and traces of hypophosphite in a matter of seconds. © 2004 Elsevier Ltd. All rights reserved.

**Keywords:** Phosphonic acid; Phosphinic acid; Methylphosphonic acid; Odor; Condensation nuclei

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## 1. Introduction

Phosphine gas (PH<sub>3</sub>, see Gmelin, 1993) is a volatile phosphorus compound which oxidizes in the terrestrial atmosphere ultimately to non-volatile and hygroscopic

phosphoric acid, a stable form of phosphorus on earth (Frank and Rippen, 1987). In Jupiter's reductive hydrogen and methane atmosphere, it is assumed that atmospheric lightning triggers the redox cycle of phosphorus between elemental phosphorus (which may be the source of red stripes and spot of Jupiter) and phosphine (Borunov et al., 1995).

It was earlier claimed that phosphorus can cycle in the atmosphere only as phosphate bound to aerosol such as plant pollen, dust and water droplets (Graham and Duce, 1979). Lewis et al. (1985) found filterable phosphorus in rain and linked it to a hypothetical volatile phosphorus compound.

On earth, phosphine has recently been found (in the  $100 \text{ pgm}^{-3}$  to  $100 \text{ ngm}^{-3}$  range) as a worldwide trace compound in remote atmosphere (Glindemann et al., 1996a,b, 2003). The observed diurnal night-time maximum of the phosphine concentration was interpreted as result of flux of phosphine into the atmosphere and subsequent daytime oxidation of phosphine. Phosphine has also been found in surface air of the Northern Sea (Gassmann et al., 1996) and in urban air of Beijing (Liu et al., 1999).

It has been speculated that the oxidation of phosphine to phosphoric acid could provide condensation nuclei for cloud formation in the upper troposphere and subsequently influence the global climate (Glindemann et al., 2003).

A review by Hudson (1993) shows that cloud condensation nuclei (CCN) knowledge is still inadequate for understanding global climate change, and suggests that the knowledge base for CCN be significantly expanded. Phosphine is at this time not on a list of anthropogenic tracers of convective processes related to clouds (Crawford et al., 2003).

It is of interest to find sources and mechanisms which could produce phosphine gas ( $\text{PH}_3$ ) and drive a volatile link of the atmospheric phosphorus cycle. Phosphine can escape into the atmosphere from industries (WHO, 1988) and from fumigation (Pratt, 1998). On the search for suspected natural biogenic emission sources of phosphine, researchers reported on phosphine in different types of biogas (Devai et al., 1988; Glindemann et al., 1996b). A microbial mechanism reducing oxidized forms of phosphorus to phosphine was claimed to be found (Devai et al., 1988; Gassmann and Glindemann, 1993; Jenkins et al., 2000). A major semi-biological or "microbially mediated" mechanism of phosphine production has been shown (Glindemann et al., 1998), comprising anaerobic bio-corrosion of phosphorus rich iron by microbial acidic and sulfide metabolites and hydrolysis of phosphide-like impurities to phosphine.

Here we present a laboratory simulation of an atmospheric lightning-chemical phosphine forming mechanism. This is energetically similar to the industrial chemical reduction of phosphate rock by carbonaceous

material (coal or natural gas) which is only possible at high temperature. The electrothermic method of P production, which comprises the reduction of molten natural phosphates with carbonaceous materials consumes much energy and will only perform at  $>1400^\circ\text{C}$  (Klimovich, 1975). But it was found, that the use of gaseous reducing agents is favorable (compared to solid carbon) in terms of lowering the process temperature and energy consumption of phosphorus production, by reducing molten natural phosphates in kilns (Klimovich, 1975). The reducing activity of the studied gases and C increases in the series:  $\text{CO} < \text{H}_2 < \text{C} < \text{CH}_4 < \text{C}_2\text{H}_4 < \text{C}_2\text{H}_2$ . Plasma conditions ( $3500\text{--}6000^\circ\text{C}$ ) were found to enable the thermal dissociation of calcium-phosphates, which would provide even more reactivity of phosphates (Burov et al., 1975).

We believe that the energetic activation of the chemical reduction of  $\text{P}(+5)$  is possible by atmospheric lightning, especially if phosphate containing biomass were struck by lightning and forms a very hot gaseous/plasma state. We also believe that methane and hydrogen are useful model substances of pyrolytic gases with high reducing power which may form if lightning strikes biomass, soil and aerosol and where air oxygen is consumed in the reducing plasma. The difficulties to measure real atmospheric lightning chemistry where outlined by Wang et al. (1998) for  $\text{NO}_x$  formation. Bossard et al. (1986) used spark discharges to simulate the combination of phosphine and methane to methylphosphine on Jupiter. Facing a similar methodical problem, we decided to simulate lightning in the laboratory by using electrical discharge experiments. As reducing agent we used methane or hydrogen or organic matter. Similar lightning simulation (Glindemann et al., 1999; De Graaf and Schwartz, 2000; Schwartz, 2004) has shown that phosphate is reduced by  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$  and organic matter.

## 2. Samples and methods

### 2.1. Reaction of phosphate salt initiated by lightning using a spark inductor

0.1 ml of an aqueous solution of  $\text{Na}_2\text{HPO}_4$  (MERCK) representing  $100 \mu\text{g}$  of phosphorus was spread over the inner surface of a 10-ml glass bulb filled with air or mixtures of methane, hydrogen and nitrogen. A spark was produced by a spark inductor commonly used for high vacuum control in glass vacuum systems (Fig. 1a). To guide the flash of the spark through the glass bulb (and not around the outside) the bulb was flattened toroidally and the inductor was placed at the narrowest point (5 mm) of the glass walls. During the reaction time of 60 s, 50 ml of methane atmosphere were flushed

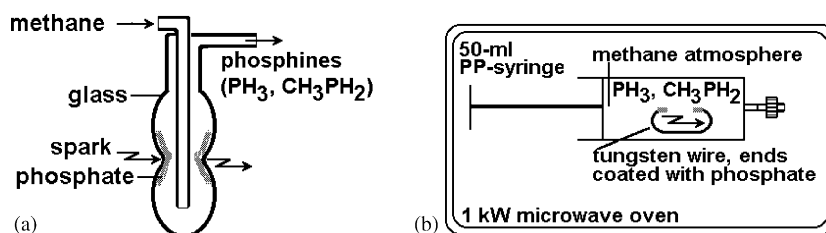


Fig. 1. Production of phosphine and methylphosphine from phosphate and methane by electrical discharge experiments simulating lightning (a) Lightning by a spark inductor, commonly used for vacuum control (discharge flow experiment). (b) Lightning by a tungsten wire inside a syringe, placed in a microwave oven (flash discharge experiment)

Table 1

Reduction of phosphate by  $\text{CH}_4$  ( $\text{H}_2$ ) to phosphine and methylphosphine by lightning experiments using spark inductor or microwave lightning. GC-measurement by NPD, FPD and MS detectors

Column 1	2	3	4	5	6	7	8
	(μg phosphine-P/kg phosphate-P) averages				reduction factor used		
	$\text{PH}_3$	$\text{CH}_3\text{PH}_2$	$\text{CH}_3\text{PH}_2$	$\text{CH}_3\text{PH}_2$			
	detector used				$\text{CH}_4$ ( $\text{H}_2$ )	Plasma	$\text{PO}_4$
Row	GC(1)/ NPD	GC(2)/ NPD	GC(2)/ FPD	GC/MS	reductant	lightning	phosphate
1	<i>Experiment using a inductor-spark lightning</i>						
2	Control of gas media used, without use of spark inductor						
3	air n.d.						
4	10% $\text{CH}_4$ in $\text{N}_2$	1			X		
5	50% $\text{CH}_4$ in $\text{N}_2$	n.d.			X		
6	100% $\text{H}_2$	1			X		
7	Controls without use of phosphate but use of spark inductor						
8	air n.d.						
9	10% $\text{CH}_4$ in $\text{N}_2$	16			X	X	
10	50% $\text{CH}_4$ in $\text{N}_2$	92			X	X	
11	Control without use of $\text{CH}_4$ ( $\text{H}_2$ ) but with use of spark inductor and of phosphate						
12	air n.d.						
13	Use of spark inductor, phosphate and reduction means ( $\text{CH}_4$ , $\text{H}_2$ )						
14	10% $\text{CH}_4$ in $\text{N}_2$	130			X	X	X
15	50% $\text{CH}_4$	20000	4100	2200	X	X	X
16	100% $\text{H}_2$	150			X	X	X
17	50% $\text{CH}_4$ , static experiment	8200			X	X	X
18	<i>Experiment using microwave-plasma lightning</i>						
19	Control of gas media used, without use of microwave						
20	100% $\text{CH}_4$	n.d.	400	390	n.d.	X	X
21	Control without use of phosphate but use of microwave						
22	100% $\text{CH}_4$	430	520	380	n.d.	X	X
23	Use of microwave lightning, phosphate and $\text{CH}_4$						
24	100% $\text{CH}_4$	620000	42000	50000	20000	X	X
25	Control, use of phosphate, microwave, no $\text{CH}_4$						
26	100% $\text{N}_2$	6200	n.d.	n.d.	n.d.	X	X

Units in mass phosphine-P ( $\text{PH}_3$  or  $\text{CH}_3\text{PH}_2$ ) liberated per mass of feed phosphate.

continuously through the bulb and sampled in a 50-ml PP one way syringe for measurement of phosphine (dynamic experiment). In one exceptional case (Table 1,

row 17) the reaction was carried out by flushing methane in five 10-ml portions between five 1-min periods of lightning (static experiment).

### 2.2. Reaction of phosphate salt initiated by lightning using microwave energy

The spark flash of the spark inductor was too small (0.1 mm thick, 5 mm long) to produce sufficient methylphosphine detectable by GC-MS. Therefore, in an additional experiment, lightning was simulated by more powerful microwave energy. 0.05 ml of aqueous solution of  $\text{Na}_2\text{HPO}_4$  (MERCK) representing 100  $\mu\text{g}$  of phosphorus were spread over the ends of a 4-cm wolfram wire of 1-mm diameter, formed to be an open loop (Fig. 1b). The wire was placed in a beaker of porcelain inside a 50-ml polypropylene disposable syringe filled with methane atmosphere. During 5 s of microwaving with a 1-kW commercial microwave device a glaring light between the ends of the wire was to be seen. The quantity of phosphine and methylphosphine in the reaction gas in the syringe was measured by GC-MS.

### 2.3. Gas chromatography

Ten millileter of the gas sample were cryo-trapped and injected into a gas chromatograph GC HP 5890 II equipped with a  $25\text{-m} \times 0.53\text{-mm}$   $5\text{-}\mu\text{m}$  CP-Sil5CB GC column (Chrompack) (see Glindemann et al., 1996a). To identify the phosphines, parallel detection was carried out with nitrogen-phosphorus detector (NPD) and flame photometric detector (FPD) in the phosphorus mode and also with GC-MS (HP MSD 5971, selected ion mode of mass peaks 45–48  $m/z$  of methylphosphine). The comparison of the GC retention times and the quantification of results was possible by using certified gas standards of phosphine and of a custom made gas standard of methylphosphine (MESSER-GRIE-SHEIM). The GC results were used to calculate the mass ratio (in  $\mu\text{g kg}^{-1}$ ) of phosphine-phosphorus liberated per mass of phosphate phosphorus (100  $\mu\text{g}$ ) fed into the experiment (Table 1).

## 3. Results and discussion

The experimental results in Table 1 show, that the small electrical discharge by a spark inductor or a microwave generator can activate the chemical reduction of phosphate by methane to phosphine and methylphosphine (rows 15, 24, columns 2–5). Omitting one of the three phosphine forming factors (phosphate as P-source, lightning as source of activation energy, or methane as reducing reagent) prevents phosphine formation.

### 3.1. Control reductant+lightning, no phosphate

Negligible control values, rows 9, 10, 22, columns 2 are explainable by phosphate impurities in the glass of the bulb.

### 3.2. Reductant+lightning+phosphate

The maximum yield of phosphine-P ( $\text{PH}_3$ ) related on the phosphate-P used was  $20,000 \mu\text{g kg}^{-1}$  (0.02% of P) using spark inductor and  $620,000 \mu\text{g kg}^{-1}$  (0.6% of P) using microwave discharge (respectively 4100 and 41,700  $\text{ng kg}^{-1}$  of methylphosphine). The variability of the measured concentrations was comparably small in spite of the badly controllable conditions in electrical discharge plasma (2...4 repetitions, about 30% deviation). High concentration of methane increases phosphine formation (rows 12–15). Hydrogen is a less potent reductant than methane in the experiment (row 16, column 2).

The odor was strongly reminiscent of the products of the hydrolysis of carbide (vinylacetylene and similar unsaturated hydrocarbons (detected) and garlic like (methylphosphine detected). The reaction gas of methane contained also hydrogen as a product.

### 3.3. Control phosphate+lightning, no reducing agent

We believe that the value 6 mg phosphine  $\text{kg}^{-1}$  phosphate (row 26, column 2), under the conditions of phosphate + lightning, no reducing agent, is caused by a plasmatic recombination mechanism. A similar result was obtained (Glindemann et al., 1999) finding up to significant 0.5% yield reduction of phosphate to phosphite in 100%  $\text{N}_2$  atmosphere. We think it likely that the high-temperature plasma—produced as a result of the discharge—contains radical ions such as P which recombine, as a result of rapid cooling, with hydrogen radicals (from dissociation of water vapor) to produce the phosphine observed.

We regard this result as a modification of the lightning-chemical mechanism, which produces phosphine without obvious reductive chemicals other than nitrogen gas present.

To investigate the effect of lightning in the real world on the reduction of phosphate contained in soil and in atmospheric aerosol (plant pollen), the microwave experiment was later repeated with 100 mg plant pollen (rape, representing about 0.5 mg P) in air atmosphere and with 0.1 g organic soil (representing about 0.3 mg P) in air atmosphere. These experiments resulted in a yield of 0.2% phosphine of total P (plant pollen) and 0.1% phosphine of total P (soil). No reducing gas ( $\text{CH}_4$ ,  $\text{H}_2$ ) was added to these samples because it was assumed that they contained more than enough carbon and hydrogen

to produce phosphate reducing conditions in microwave plasma.

### 3.4. Review of reduced phosphorus species found with the reported lightning method

These reported results correspond with similar lightning simulation that has shown, that  $\text{PO}_4$  is reduced by 10%  $\text{CH}_4$  in  $\text{N}_2$  to  $\text{PO}_3$  at a yield of 11%, plus traces of  $\text{PO}_2$  (Glindemann et al., 1999), by  $\text{H}_2$  and  $\text{CO}$  to  $\text{PO}_3$  at a yield of up to 25%, and 0.5%  $\text{PO}_3$  in 100%  $\text{N}_2$  (DeGraaf and Schwartz, 2000), by 100%  $\text{CH}_4$  to methylphosphonic acid at a yield of up to 8.5% and by condensed organic matter to 5% methylphosphonic acid (Schwartz, 2004).

Altogether, laboratory lightning (literature and present work) was able to reduce a significant portion of phosphate to phosphite, methylphosphonic acid, hypophosphite, phosphine, and methylphosphine in a matter of seconds (see their formulas in Fig. 2 assuming that these species would appear as phosphines and as oxyacids of phosphorus).

We suggest the following mechanism of plasma-chemical phosphate reduction to phosphine and of the subsequent formation of methylphosphine: The electrical discharge produces hot plasma containing reactive atomic and molecular radicals which originate from the reaction components methane or hydrogen, as well as by volatilization of the target solid phosphate and of its solvent water. We estimate that the temperature of the sample may have approached 3000 K (tungsten wire did partially evaporate). The produced phosphine can react with methylradicals to form methylphosphine. The formed reaction products are stabilized and trapped by rapid cooling when they are purged out of the plasma or at least when the plasma terminates. Therefore, the yield of the static experiment (Table 1, row 17) in spite of five times longer discharge time was smaller than the yield of the dynamic experiment (row 15) where the reaction

products are allowed to escape from the plasma. Although we have thus far only been able to systematically examine materials containing relatively high proportions of phosphate, we are encouraged to think that phosphorus present in most common soils, biomasses and atmospheric aerosols, which typically contain 0.1–0.5%  $\text{P}_2\text{O}_5$ , might be similarly reduced.

Plant pollen and soil phosphate on the other hand, was reduced in the microwave plasma to phosphine even in the presence of air atmosphere, however at a much lower yield compared to the phosphate salt. We think that even in the oxic earth's biosphere organic matter struck by lightning could form reducing plasma in which oxygen is eliminated by local excess of activated carbon or hydrogen and phosphate is reduced. To test this hypothesis more thoroughly, a more powerful lightning device is necessary delivering the high energy to atomize biomass of soil and wood at larger scale to produce a more homogeneous reducing plasma, which is less penetrated by atmospheric oxygen.

We suggest the following combinations of factors which would produce phosphine in the real environment:

*Electrical discharges* (Atmospheric lightning, ball lightning, volcanic lightning);

*Phosphorus* (any form of phosphorus, such as phosphate, phosphonate, phosphinate, in minerals, soil, water and its biospheres, atmospheric aerosol, volcanic aerosol, which is in the order of 0.1–0.5%, Koritnig, 1978);

*Chemical reduction means* (the carbon, hydrogen and their compounds in soil, water and its biospheres, in atmospheric aerosol; the methane content in the atmosphere (1 ppm);  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{H}_2\text{S}$  in volcanic gases (Symonds et al., 1994).

*The suggested locations of the phosphine producing reactions are:* Volcanic eruption clouds (providing intense lightning combined with high concentration of target aerosol and volcanic gases); the plasma of

Phosphoric acid, (forming phosphates),	7664-38-2	$\begin{array}{c} \text{HO} \\   \\ \text{HO}-\text{P}=\text{O} \\   \\ \text{HO} \end{array}$
Phosphonic acid (forming phosphites),	13598-36-2	$\begin{array}{c} \text{HO} \\   \\ \text{HO}-\text{P}=\text{O} \\   \\ \text{H} \end{array}$
Phosphinic acid (forming hypophosphites),	6303-21-5	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{P}=\text{O} \\   \\ \text{HO} \end{array}$
Phosphine, 7803-51-2		$\text{PH}_3$
Methylphosphonic acid, 993-13-5		$\begin{array}{c} \text{HO} \\   \\ \text{CH}_3-\text{P}=\text{O} \\   \\ \text{HO} \end{array}$
Methylphosphine, 593-54-4		$\text{CH}_3-\text{PH}_2$

Fig. 2. CA-Names, CAS numbers and formulas of reduced phosphorus compounds which were produced by laboratory lightning in the presence of phosphate and reducing agents such as  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{CO}$ . Phosphine and methylphosphine (gases) were detected in the present paper. The remaining phosphorus compounds (condensed matter) are reviewed data (Glindemann et al., 1999; De Graaf and Schartz, 2000).



lightning striking the ground, the plasma channel of atmospheric lightning; the path of ball lightning.

*We expect odor and taste sensations near the location of lightning caused by phosphines:* The human sense of smell is not anymore a very popular sensor in chemistry due to the existence of gas chromatography. However, the nose may be the most common sensor at hand once lightning strikes randomly to detect that suspected lightning phosphorus chemistry. The most recognized atmospheric chemical products of lightning are nitrous oxides ( $\text{NO}_x$ ) and ozone (Wang et al., 1998), which cause an odor described as “electric”, ozone, pungent, acrid (Brand, 1923; Barry, 1980; Singer, 1971). In addition, odor descriptors such as sulfur, rotten eggs, rotten cabbage, and garlic have been reported (Brand, 1923). We did not add sulfur and did not have the ability to analyze  $\text{H}_2\text{S}$  and methylsulfides in our lightning experiment. But we believe that these thermodynamically more favorable (compared to phosphorus) sulfur compounds have a good chance to be produced by environmental lightning and cause odor due to their very low odor threshold in the  $0.001 \text{ mg m}^{-3}$  concentration range.

*Mouthfeel sensation by phosphine:* Pure phosphine has, to our knowledge, no odor (Fluck, 1976). However, we experienced and also heard of a “dry mouth”, “mouthfeel” or “metallic” taste sensation by phosphine at the  $1 \text{ mg m}^{-3}$  level.

*Garlic odor by methylphosphine:* When methylphosphine is formed, this phenomenon would be accompanied by a garlic like odor of the air near the lightning. Using olfactometry we found methylphosphine having an extremely low odor threshold of  $6 \text{ ng P m}^{-3}$  or in other words,  $6 \text{ mg}$  of methylphosphine formed by lightning would make  $1 \text{ million m}^3$  of air, a cube of  $100 \text{ m}$ , just detectable.

*Carbide odor by unsaturated hydrocarbons:* The odor of the reaction gas was strongly reminiscent of the products of the hydrolysis of carbide, such as vinylacetylene and similar unsaturated hydrocarbons which were detected.

*Lightning as a source of organophosphorus compounds:* Methylphosphine is a very reactive reagent but its stable C-P bond would survive transformations in form of the oxidation product methylphosphonic acid (Kosolapov, 1950). Methylphosphonic acid, which has been even more efficiently formed by direct reduction and combination of phosphate with methane and organic material (Schwartz, personal communication, 2004) could interfere with the chemical traces of manufacture and use of phosphororganic warfare agents controlled by CWC (1993).

Heterogeneous lightning chemical reduction of lithospheric phosphate to phosphine, methylphosphine and phosphite might also be possible in the methane containing atmosphere of moons of the gas planets or has been possible on the prebiotic earth. The results support earlier

theories which require phosphine (Raulin and Ponnamparuma, 1981) and C-P compounds (De Graaf et al., 1995) on the archaic earth as mobile and soluble phosphorus which is important for the initiation of life.

Regarding the annual production flow of phosphine into the atmosphere, we try a simple comparison. Wang et al (1998) calculate for a lightning frequency of  $100 \text{ flashes s}^{-1}$  a global NO production of  $8.3 \text{ Tg (N)}$  or  $8.3 \text{ million tons year}^{-1}$ . If we simply assume that lightning produces 10,000 times less phosphine compared to NO, because of the more limited presence of phosphorus and reductive chemicals, this would result in  $830 \text{ tons phosphine year}^{-1}$  or  $0.26 \text{ g PH}_3$  per flash. By contrast, the industrial production of phosphine was only  $0.386 \text{ tons year}^{-1}$  ( $300\,000 \text{ liters}$ ) worldwide as a dopant and  $37 \text{ tons year}^{-1}$  in Germany as a fumigant (WHO, 1988).

The volume of the global atmospheric boundary layer ( $2.5 \text{ km}$ ,  $5.1 \times 10^8 \text{ km}^2$ ) is  $1.28 \times 10^{18} \text{ m}^3$ . The amount of phosphine necessary to build up  $0.1 \text{ ng m}^{-3}$   $\text{PH}_3$  is  $0.128 \times 10^{18} \text{ ng}$  or  $128 \text{ tons P}$  as phosphine, if it is assumed to be stable. We know from the diurnal disappearance and reappearance of phosphine in the lower troposphere (Glindemann et al., 1996a), that a daily constant flow of phosphine is necessary to keep phosphine at this measurable level. However, in the upper troposphere (Glindemann et al., 2003), phosphine was found in bright daylight, and may survive for more than a day as a very mobile carrier of phosphorus.

#### 4. Conclusions

- Simulated lightning (spark produced by spark inductor or microwave), methane gas and condensed organic matter proved to be effective for the reduction of phosphate to phosphine and methylphosphine.
- Phosphine and methylphosphine could reveal their production by garlic like odor if lightning strikes organics-rich soils.
- Reduced oxy-acids of phosphorus are the dominant products of simulated lightning. The reviewed data of the yield of simulated lightning-chemical phosphate reduction range from 25% (phosphite, by 18%  $\text{H}_2 + \text{CO}$ ), 11% (phosphite, by 10% methane, Glindemann et al., 1999), 8.5% respectively 5% (methylphosphonic acid, by 100% methane, respectively, condensed organic matter, Schwartz, 2004) down to 0.06% (phosphine) and 0.002% (methylphosphine).
- Reduced oxides of phosphorus will dominate lightning chemistry as well in the real oxygen-rich atmosphere.
- Condensed organic matter is an alternative reductant to methane in phosphate reduction, which is similar to successful use of coal or natural gas in the

phosphorus industry. Organics rich soil which is struck by lightning will likely produce chemically reducing conditions.

- The finding of phosphite (yield 0.5%, Glindemann et al., 1999) and phosphine (yield 6 mg kg<sup>-1</sup>) in blank samples indicates a plasmatic recombination mechanism allowing phosphate reduction even if no reducing chemical is present, though, no oxygen was present in the experimental gas mixture.
- Future research using more powerful equipment may very well prove that atmospheric lightning chemistry is important for the atmospheric cycling of phosphine and for additional chemically reduced phosphorus compounds such as methylphosphine phosphite (phosphonic acid), hypophosphite (phosphinic acid), and methylphosphonic acid.
- Specifically, it would be interesting to see what a real lightning strike could do in phosphorus rich soils. Could it trigger a massive emission of phosphine? Does phosphine contribute to the energy sorption of the atmosphere? Or does rather its ultimate oxidation product, particles of phosphoric acid, do more to the climate as a “catalyst” of cloud formation?
- It is still not sure if phosphine has any significant repercussions for aerosol, cloud, or climate issues given the dominance of other mineral, organic, and sulfate aerosol. It would be interesting to weigh the importance of phosphine for atmospheric chemistry in addition to its atmospheric concentration by other properties like possible significant mobility (Glindemann et al., 2003) in the atmosphere.
- There are clearly some interesting trends in phosphine between the surface and upper troposphere that are not easily explained. If the sources and fate of phosphorus can be better understood, it is possible that phosphine may become a valuable tracer for air associated with lightning activity or continental convective processes or whatever process is found to ultimately drive the distribution of phosphine in the atmosphere.

## Acknowledgements

Centre for Environmental Research Leipzig-Halle Ltd. (joint project 08/95). Partially supported, by NSF (Grant No. BES-0201849). Opinions expressed are those of the authors and not necessarily those of the Foundation. A.W. Schwartz and K.P. Thiessen (consultation).

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